

Vulcanization of Saturated Acrylic Resins

Rubberlike materials, designated as Lactoprene, were prepared in earlier investigations by copolymerizing ethyl acrylate with small proportions of butadiene, isoprene, or allyl maleate, compounding the resulting copolymers (assumed to have olefinic unsaturation) with sulfur and accelerators, and then curing the compounded products. Since it was difficult to prevent cross linkage during polymerization of mixtures containing butadiene and other polyfunctional monomers, vulcanization of acrylic resins not having olefinic linkages was attempted. Polyethyl acrylate and various saturated copolymers of ethyl acrylate were vulcanized satisfactorily with red

lead and quinone dioxime and also with benzoyl peroxide. The copolymers made from acrylonitrile, cyanoethyl acrylate, chloroethyl acrylate, chloropropyl acrylate, and phenyl acrylate were vulcanizable with certain sulfur-accelerator mixtures. The preparation of rubberlike materials by vulcanizing saturated acrylic resins instead of copolymers of the ethyl acrylate-butadiene type has the following advantages: (a) Agents and techniques to prevent cross linkage are not required; (b) the polymers and copolymers are soluble, and hence the viscosity of the solutions can be used as an index of the molecular weight; and (c) synthetic rubber cements can be made.

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THE vulcanization of copolymers (presumed to have olefinic unsaturation) made from alkyl acrylates and small proportions of butadiene, isoprene, allyl maleate, and similar polyfunctional monomers are described in other papers (4, 9). Although the vulcanizates prepared in this manner were rubbery and seemed suitable as rubber replacements in some fields, polyfunctional monomers were generally objectionable because of their tendency to create cross linkages prematurely—that is, during polymerization. After a study of the copolymerization of ethyl acrylate with many polyfunctional compounds had indicated that cross linkage (or effects ordinarily attributed to it) nearly always occurs when this method is used to produce unsaturated copolymers, it was decided to attempt the vulcanization of saturated acrylic resins.

Although olefinic unsaturation has generally been considered necessary for vulcanization (10), it seemed likely that vulcanization could be effected through some combination of a nonolefinic functional group (ester, cyano, halogen, etc.) and a vulcanizing agent. Acrylic resins contain ester groups and one hydrogen alpha to the carboxyl group that might enter into cross linkage or vulcanization reactions. Acrylic resins containing other functional groups were prepared by copolymerizing ethyl acrylate with small proportions of acrylonitrile, β -cyanoethyl acrylate, γ -chloropropyl acrylate, and similar monomers. Vulcanization of these copolymers was attempted with various recipes including benzoyl peroxide and reinforcing agents, sulfur and organic accelerators, *p*-quinone dioxime and red lead, *p*-dinitrobenzene and litharge (13), sulfur and litharge, and Polyac (14). The results of this study and certain properties of vulcanizates prepared from saturated acrylic resins are given in the present paper.

The polymerizations were carried out as before (4, 9) in round-bottom, three-neck, Pyrex flasks fitted with a thermometer well, reflux condenser, and water-sealed stirrer (ground-glass joints). Steam was passed through the emulsion to distill monomer or volatile impurities, and then coagulation was effected by the addition of a dilute solution of sodium chloride. The polymers were washed with water on a small washing mill and air-dried.

The acrylic esters were emulsion-polymerized more successfully when proper consideration was given to purity of the monomer and the threshold or minimum catalyst concentration required for polymerization. The threshold catalyst concentration was related to the temperature, and only small amounts of catalyst (ammonium persulfate) were needed under refluxing conditions (approximately 82° C.). The monomers should be freshly

distilled and, if not used immediately, stored so that the formation of peroxides is minimized. The removal of inhibitors by dilute sodium hydroxide should be followed by several washings with distilled water, dilute sulfuric acid (0.01%), and finally with distilled water.

Generally it is disadvantageous to use more than the threshold concentration of ammonium persulfate. When there is too much catalyst, refluxing may be so violent that the emulsion coagulates. When the catalyst concentration is below the threshold value, polymerization may not occur even after hours of refluxing. When carried out properly, polymerization proceeds smoothly at refluxing temperature with little heating. A steam bath is more satisfactory than a water bath for this type of polymerization.

The phenyl (3), chloropropyl, methoxyethyl, cyanoethyl, and nitroisobutyl acrylates were prepared in connection with other investigations (11).

The compounding ingredients were milled into the polymers on a small rubber mill. The polymers usually were tacky and easily milled without the addition of plasticizers or softeners. Benzoyl peroxide (Luperco A) was so active as a vulcanizing agent that it was difficult to prevent scorching on the mill, even when the peroxide was incorporated last.

The compounded mixtures were cured in stainless-steel sandwich molds having the dimensions 4 × 4 × 0.032 inch or 6 × 6 × 0.075 inch. Cellophane sheets were used in the smaller mold. These were apparently detrimental, since in some instances the tensile strengths were lower.

Unlike the copolymers (4, 9) prepared with monomers having two or more olefinic linkages, most of the copolymers of the present work were soluble in organic solvents before vulcanization. The viscosities of solutions containing about 0.05 gram of polymer per 100 ml. of toluene were determined at 25° C. (constant-temperature bath) with modified Ostwald tubes. The natural logarithm of the relative viscosity divided by the concentration—that is, $(\ln \eta_r/c)$ —was used as an index of the average molecular weight of the polymers (6). It was shown experimentally that the values for $(\ln \eta_r/c)$ were approximately the same when c was 0.05 or extrapolated to 0.

VULCANIZATION OF POLYETHYL ACRYLATE

Polyethyl acrylate, prepared as shown in Table I, was compounded by several different recipes and molded at 298° F. (Table II). The sulfur-Captax-Tuads combination gave unsatisfactory

Table I. Preparation of Ethyl Acrylate Copolymers by Emulsion Polymerization

Expt. No.	Ethyl Acrylate, Grams	Copolymerizing Monomer, Grams	Tergitol Penetrant No. 4 ^a , Grams	Water, Ml.	Ammonium Persulfate, Gram	Temp., °C.	Time, Hr.	Yield, %	$\ln \eta_r/c$
1	150 ml.	None	4	300	0.025	80-92	1.5	87.5	3.82
2	142.5	Acrylonitrile, 7.5	4	250	0.02	78-92	4.25	88.5	3.96
3	142.5	Acrylonitrile, 7.5	4	300	0.045	78-91	4.5	90.5	3.82
4 ^b	1470.0	γ -Chloropropyl acrylate, 75	28	3200	0.02	81-90	1.25	...	3.91
5	142.5	β -Chloroethyl acrylate, 7.5	4	300	0.015	78-92	1.5	90	2.98
6	135	β -Chloroethyl acrylate, 15	4	300	0.015	82-91	2	88	3.24
7	89	β -Chloroethyl acrylate, 5; acrylonitrile, 6	3	150	0.12	78-91	1.75	92	5.27
8	142.5	Benzyl acrylate, 7.5	4	250	0.03	78-92	2	91	3.53
9	95	Phenyl acrylate, 5	3	150	0.1	75-92	0.83	90	...
10	142.5	β -Methoxyethyl acrylate, 7.5	4	300	0.03	80-92	1.33	93.5	Insol.
11	142.5	β -Cyanoethyl acrylate, 7.5	4	300	0.03	80-92	1.67	91	3.64
12	142.5	2-Me-2-nitro-1-propyl acrylate, 7.5	4	300	0.02	77-92	1.67	91	4.66

^a Sodium alkyl sulfate.^b Triton 720 (8 grams) used; this emulsifier is a sodium salt of aryl alkyl polyether sulfonate (15).

results, but the Lupercio A (benzoyl peroxide) and GMF (quinone dioxime) recipes gave good vulcanizates. About 4 hours at 298° F. was necessary for vulcanization with the quinone dioxime formula, and the vulcanizates thus prepared (Tables II and III) had moderately high tensile strengths. Cross linkage occurred much more rapidly with benzoyl peroxide (10 to 20 minutes at 210° F.), but the products were relatively weak. [Cross-linked acrylic resins were produced also by preparing ethyl acetate solutions of the polymeric acrylic ester and benzoyl peroxide (Lucidol), applying the solution to a surface, allowing the solvent to evaporate, and heating the resulting film at about 80° C. for a short time.]

alpha to the carboxyl group, possibly cross linkage occurs through the same type of coupling.

VULCANIZATION OF ETHYL ACRYLATE COPOLYMERS

Ethyl acrylate was copolymerized with various monomers (Table I), and the resulting copolymers were compounded by different recipes and molded to ascertain whether the cyano, halogen, phenyl, ether, and nitro groups in the copolymers would facilitate vulcanization. The results show that several functional groups in the acrylate copolymers are susceptible to cross linkage or vulcanization. It has been believed that olefinic

Table II. Vulcanization of Polyethyl Acrylate and Ethyl Acrylate Copolymers^a

Expt. No.	Copolymerizing Monomers, %	Compounding Recipe	Curing Time at 298° F., Min. ^b	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product	Brittle Point, °C.
1	None	Quinone dioxime ^c	240	1390	510	55	710	-16
		Benzoyl peroxide ^d	120	810	440	46	355	-16
		Sulfur ^{e,f}
2	Acrylonitrile, 5	Quinone dioxime ^c	240	1320	260	72	345	-11
		Benzoyl peroxide ^d	180	1000	420	53	420	-7
		Sulfur ^e	240	830	1040	50	860	-7
3	Acrylonitrile, 5	Quinone dioxime ^c	240	1420	340	70	480	-9
		Benzoyl peroxide ^d	120	870	520	52	450	-8
		Sulfur ^{e,f}
4 ^g	γ -Chloropropyl acrylate, 4.8	Quinone dioxime ^c	150 ^h	1610	470	67	756	...
		Sulfur ^e	210 ⁱ	1240	950	39	1178	...
5	β -Chloroethyl acrylate, 5	Quinone dioxime ^c	120	1610	400	64	645	-15
		Benzoyl peroxide ^d	240	870	500	45	435	-9
		Sulfur ^e	240	1280	880	46	1125	-15
6	β -Chloroethyl acrylate, 10	Quinone dioxime ^c	180	1350	460	56	620	-15
		Benzoyl peroxide ^d	120	1050	280	50	295	-11
		Sulfur ^e	180	1220	720	42	880	-14
7	β -Chloroethyl acrylate, 5; acrylonitrile, 6	Quinone dioxime ^c	240	1180	470	56	555	-5
		Benzoyl peroxide ^d	180	820	560	45	460	-6
		Sulfur ^{e,f}
8	Benzyl acrylate, 5	Quinone dioxime ^c	240	1410	480	65	675	-11
		Benzoyl peroxide ^d	120	640	490	45	315	-10
		Sulfur ^e	240	<100	>2400	40
9	Phenyl acrylate, 5	Quinone dioxime ^c	240	960	180	75	170	-17
		Benzoyl peroxide ^d	20	570	480	42	275	-11
		Sulfur ^e	240	790	780	50	615	-16
10	Methoxyethyl acrylate, 5	Quinone dioxime ^c	240	1090	340	55	370	-17
		Benzoyl peroxide ^d	80	<100	380	40
		Sulfur ^e	240	<100	680	39
11	β -Cyanoethyl acrylate, 5	Quinone dioxime ^c	120	1670	450	65	750	-15
		Benzoyl peroxide ^d	80	510	440	45	225	-13
		Sulfur ^e	120	1090	860	48	940	-16
12	2-Me-2-nitro-1-propyl acrylate, 5	Quinone dioxime ^c	120	470	410	31	190	-14
		Benzoyl peroxide ^d	180	760	440	41	335	-13
		Sulfur ^{e,f}

^a Prepared as described in Table I; brittle points of vulcanizate determined as described in citation (12).^b Cured in 4 × 4 × 0.032 inch molds.^c Compounded: polymer, 100; red lead, 10; quinone dioxime, 2; zinc oxide, 5; stearic acid, 3; Furnex Beads (semireinforcing carbon black), 30.^d Compounded: polymer, 100; iron oxide, 150; Lupercio A (benzoyl peroxide), 5.^e Compounded: polymer, 100; Captax (mercaptobenzothiazole), 0.5; zinc oxide, 10; stearic acid, 2; sulfur, 2; Furnex Beads, 30; Tuads (tetramethylthiuram disulfide), 1.^f Specimen unsatisfactory for testing.^g Cured at 303° F.^h Cured in 6 × 6 × 0.075 inch molds.ⁱ Cured at 312° F.

Table III. Preparation and Vulcanization of Copolymers of Ethyl Acrylate with Chloropropyl Acrylate or Chloroethyl Acrylate^a

Expt. No.	Copolymerising Monomer, Grams	Ethyl Acrylate, Grams	Water, Ml.	Tergitol Penetrant No. 4, Grams	Triton 720, Grams	Ammonium Persulfate, Grams	Time, Hr.	Temp., °C.	Curing Conditions Min. °F.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	$\ln \eta_r/c$
1	γ -Chloropropyl acrylate, 32	630	1125	5	..	1.70	5	65-92	180 298	500	1030	42	3.023
2 ^b	Same, 10	90	300	4	..	0.04	3.5	75-92	240 298	990	760	42	4.784
3 ^c	Same, 44	882	3050	40	..	0.05	1	81-88	180 ^d 298	1700	480	68	5.386
4 ^c	Same, 45	897	2860	40	..	0.03	1	80-84	240 298	1200	620	59	
5	Same, 150	3000 ml.	5000	60 (paste)	80	0.180	4.5	82-90	240 298	1510	710	48	...
6	Same, 150	3000 ml.	6000	60 (paste)	30	0.040	3	83-90	180 ^d 298	1940	420	76	
7	Same, 75	1470	3200	28	8	0.020	2	78-90	210 312	1240	950	39	5.273
8	Same, 200	4000 ml.	5000	80 (paste)	40	0.035	3	82-90	150 ^d 303	1610	470	67	
9	β -Chloroethyl acrylate, 125	2375	5000	45	12.5	0.355	6.5	82-88	120 ^d 298	1610	560	63	5.062
10	Same, 25	475	1000	9	2.5	0.215	..	82-88	180 298	1210	790	48	
11	Same, 20	380	800	4	2	0.010	1.25	82-91	240 298	1440	840	42	2.829
12	Same, 60	1140	2700	30	15	0.015	2.25	81-92	240 298	1430	860	48	3.255
13	Same, 50	950	2250	30	..	0.16	4.5	78-82	240 298	740	800	48	5.079
14	Same, 25	500	1350	10	..	0.100	2	75-92	240 298	1120	820	45	1.968
									180 ^d 298	1300	530	48	3.284

^a Compounded with sulfur and accelerators (footnote ^a of Table II) unless otherwise indicated.

^b Methyl acrylate (30 grams) and *n*-butyl acrylate (70 grams) were also used as co-monomers.

^c The copolymers prepared in experiments 3 and 4 were combined.

^d Compounded with quinone dioxime and red lead (footnote ^a of Table II).

unsaturation is necessary for vulcanization with sulfur, but our findings indicate that cyano, halogen, and phenoxy groups are also adequate in acrylic resins when suitable vulcanization agents are used. We have not ascertained whether these groups are susceptible to vulcanization in the absence of ester groups such as those found in acrylic resins.

The cyano group in the acrylonitrile copolymer did not decrease the time required for quinone dioxime vulcanization (experiments 2 and 3, Table II) or significantly improve the properties of the vulcanizates. It was possible, however, to vulcanize the acrylonitrile copolymer with sulfur. The acrylonitrile segments in the polymer chain raised the brittle point and increased the hardness.

The cyano group in the cyanoethyl acrylate copolymer was advantageous. It decreased the time required for vulcanization with quinone dioxime and permitted sulfur vulcanization (experiment 11, Table II). It did not appear to raise the brittle point.

Acrylic resins containing halogen were prepared by using either γ -chloropropyl or β -chloroethyl acrylate as copolymerizing monomers. The halogen in the polymers was beneficial in that it decreased the time required for the quinone dioxime vulcanization and resulted in good sulfur vulcanizates. Moreover, it did not adversely affect the brittle points of the vulcanizates. Copolymers made from ethyl acrylate and either chloroethyl or chloropropyl acrylate have been prepared several times in this laboratory and given considerable study (Table III).

The phenyl group of benzyl acrylate seemed ineffective for vulcanization purposes, but the phenyl group of phenyl acrylate permitted sulfur vulcanization. The quinone dioxime and benzoyl peroxide vulcanizates prepared from the phenyl acrylate polymers were unsatisfactory, perhaps because of the antioxidant character of the phenyl ester group.

Vulcanizates of poor quality were obtained from the resins containing the ether and nitro groups (Table II). The possibility that molecular weight as well as specific effects of functional groups was responsible for the differences in properties of the vulcanizates of Table II is discussed below.

EFFECT OF MOLECULAR WEIGHT

Ethyl acrylate was emulsion-polymerized under various conditions to obtain polymers of different molecular weight (Table IV). Polymers of relatively high molecular weight (as indicated by viscosity measurements) could be prepared conveniently by refluxing the reaction mixture and using low concentrations of ammonium persulfate (experiment 6, Table IV). The $(\ln \eta_r/c)$ values ranged from 2.6 to 6.3, an indication that the polymer of experiment 6 had an average molecular weight considerably higher than that of the polymer of experiment 1.

The vulcanizates prepared from the seven polymers of Table IV were roughly similar in spite of the considerable differences in average molecular weight. These results suggest that the plateau of the curve showing the relation between the properties and molecular weight (8) has been reached for polyethyl acrylate and that further increase in molecular weight would not be beneficial from the standpoint of tensile strength, ultimate elongation, and Shore A hardness.

Viscosities of toluene solutions of most of the copolymers shown in Table I were determined to ascertain whether the monomers used with ethyl acrylate had a pronounced effect on molecular weight. Moreover, it was hoped that viscosity data would indicate whether the properties of the vulcanizates (for example, the low tensile strength of the nitroisobutyl acrylate product, item 12 in Table III) could be attributed to differences in molecular weight. Since a copolymer having $(\ln \eta_r/c)$ value as low as 2.43 (experiment 7, Table I) gave a satisfactory vulcanizate and the other copolymers had even higher $(\ln \eta_r/c)$

Table IV. Emulsion Polymerization^a of Ethyl Acrylate and Properties of the Vulcanizates^b

Expt. No.	Ethyl Acrylate, Grams	Tergitol Penetrant No. 4, Grams	Temp., °C.	Time, Hr.	Ammonium Persulfate, Grams	$(\ln \eta_r/c)$	Tensile strength, lb./sq. in.	Ultimate elongation, %	Tensile product	Shore A hardness
1	680	30	72-81	0.5	0.30	2.578	1220	520	634	53
2 ^d	540	20	66-7	3	0.45	3.020	1370 ^e	560	710	52
3	550	20	62-75	0.5	0.43	2.552	1290	480	620	60
4	955	30	62-90	0.75	0.60	4.110	1330	480	638	61
5	835	30	62-85	0.5	0.50	4.285	1280	480	626	53
6 ^f	200	3	82-92	1.25	0.008	6.284	1380	480	658	58
7	760	60	62-81	0.75	0.70	4.367	1400	470	658	53

^a Except where indicated, 2 liters of water were used; polymerization yields were 89 to 99%.

^b Compounded: polyethyl acrylate, 100; red lead, 10; zinc oxide, 5; stearic acid, 3; GMF, 2; and Furnox Beads, 30; curing time was 4 hours at 298° F.; molded specimens were 4 × 4 × 0.032 inch.

^c Viscosities determined with solutions containing approximately 0.05 gram per 100 ml. of toluene.

^d 4.15 liters of water used.

^e Cured for 3 hours at 298° F.

^f 800 ml. of water used.

Table V. Vulcanization of Polyethyl Acrylate^a

Expt. No.	Cure at 298° F., Min.	Parts per 100 Polymer Red lead	Furnex Beads	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product
1	300	5	1	30	1190	360	428
2	240	5	2	30	1190	49	784
3	300	10	1	30	1110	360	400
4	180	10	2	30	1240	55	755
5	240	10	2	40	1230	63	492
6	240	10	2	50	1360	70	598

^a Prepared in experiment 5, Table III. Compounded: polymer, 100; stearic acid, 3.0; ZnO, 5.0; test specimens were 4 × 4 × 0.032 inch.

values, it appears that some specific effect of the functional group was more important than molecular weight.

The methoxyethyl acrylate copolymer was not completely soluble in toluene. Whether this was due to cross linkage or was characteristic of this particular copolymer is not known.

VULCANIZATION WITH QUINONE DIOXIME

The effects of variations in the quinone dioxime (GMF) recipe were studied briefly because this vulcanization method produced satisfactory vulcanizates with polyethyl acrylate and several ethyl acrylate copolymers. Moreover, vulcanization could be achieved in less time with quinone dioxime than with sulfur. Harder and less elastic vulcanizates were obtained by using 1 instead of 2 parts of quinone dioxime (Table V). Use of 5 parts of red lead rather than 10 softened the vulcanizate without causing any significant decrease in tensile strength. The effect of larger proportions of Furnex Beads is shown by experiments 4, 5, and 6, Table V. The vulcanizate prepared with 50 parts of black was harder and stronger but less elastic than the standard vulcanizate (experiment 4) having 30 parts of black.

Pitting sometimes occurred when curing temperatures higher than 298° F. were used. In some instances pitting at 307° F. was not severe, but badly pitted vulcanizates were produced at 312° F. Some of the undercured specimens prepared at 298° F. were pitted, although the vulcanizates cured for a longer time at this temperature were satisfactory. Possibly the tendency of products compounded with the quinone dioxime recipe to pit at temperatures much above 298° F. is related to the exothermic reaction between the dioxime and red lead (1). Products compounded according to the sulfur-Rotax-Tuads recipe showed less tendency to pit, and satisfactory vulcanizates were prepared at temperatures as high as 320° F. (75 pounds steam pressure).

EFFECT OF CARBON BLACK

In a preliminary study of the effect of carbon black, it was observed that greater tensile strengths were obtained when Kosmos, Gastex, and Pelletex were used (50 parts per 100 parts of polymer) instead of Furnex Beads. The elongation and hardness values, however, were less:

Expt. No. ^a	Carbon Black	Modulus, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product
1	Furnex Beads	970(500%)	1200	620	59	744
2	Kosmos 40	1450(500%)	1530	540	57	826
3	Dixie 20	1110(600%)	1130	610	51	689
4	Gastex		1450	490	55	710
5	Pelletex	1130(400%)	1410	530	54	747

^a Copolymer was prepared from 95% ethyl acrylate and 5% chloropropyl acrylate. Compounded: copolymer, 100; Rotax, 0.5; ZnO, 10; stearic acid, 2; sulfur, 2; Tuads, 1; and semireinforcing black, 50. Cured in 4 × 4 × 0.032 inch molds at 298° F. for 4 hours.

EFFECT OF MONOMER STRUCTURE

Vulcanizates of polymethyl acrylate were harder, stronger, and less rubbery than those prepared from polyethyl acrylate. The samples of vulcanized polymethyl acrylate had brittle points of approximately 0° C. Poly-*n*-butyl acrylate, prepared under the conditions shown in Table I, was softer and tackier than

polyethyl acrylate. When compounded with quinone dioxime formula (footnote^c, Table II) and cured for 60 minutes at 298° F., a vulcanizate with the following properties was obtained: tensile strength, 780 pounds per square inch; ultimate elongation, 640%; Shore A hardness, 47; tensile product, 500; and brittle point, about -50° C. (-58° F.).

HEAT AGING

Vulcanizates prepared by the sulfur and quinone dioxime recipes were heated in an oven at 150° C. for periods up to 5 weeks and examined to determine their resistance to aging at elevated temperatures. Heat increased the tensile strength and hardness of both vulcanizates but decreased the elongation and permanent set:

Sample ^a	Aged at 150° C., Days	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Permanent Set—10 min., 75% elongation	Set—At break
1 ^b	0	1680	370	65	25.5	20.4
	1	2170	260	81	..	22
	2	2130	200	84
	4	2240	190	83
	8	1930	90	89
2 ^c	0	1700	480	68	7.1	..
	1	2100	110	82	2.4	..
	4	2430	80	80	10.0	..
	7	2330	50	92	3.1	..
	14	2120	50	97	0	..
	21	2150	80	98
	28	2200	40	100
	35	2320	60	98

^a Specimens were heated in an oven at 150° C.; they were tough instead of brittle at end of test.

^b Polymer prepared in experiment 7, Table IV. Compounded: polymer, 100; red lead, 10; ZnO, 5; stearic acid, 3; quinone dioxime, 2; Furnex Beads, 30. Cured 240 minutes at 298° F. in 6 × 6 × 0.075 inch molds.

^c Polymer prepared in experiments 3 and 4, Table III. Compounded: polymer, 100; Rotax, 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; Tuads, 1; Furnex Beads, 30. Cured at 298° F. in 6 × 6 × 0.075 inch molds.

These results show that vulcanized acrylic resins are rather resistant to heat, and suggest that acrylic resins might be useful where rubbery materials are required to withstand relatively high temperatures. It should be possible to improve the heat-aging characteristics of vulcanized acrylic resins by making appropriate changes in the compounding recipe. These changes might include the use of antioxidants, softeners or plasticizers, decreasing the proportion of sulfur and vulcanizing agents, and loading with more suitable reinforcing agents.

BLENDS WITH OTHER SYNTHETIC ELASTOMERS

A copolymer made from ethyl acrylate and 5% γ -chloropropyl acrylate blended readily with Butyl rubber on a small rubber mill. Increasing the proportion of Butyl rubber increased the tensile strength and lowered the brittle point:

Expt. No. ^a	Butyl Rubber, % of Gum ^b	Cure at 298° F., Min.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product	Brittle Point, ° C.
1	0	180	500	1030	42	513	-16
2	20	240	1050	830	46	870	-22
3	35	240	1370	900	48	1230	-43
4	60	120	1410	920	40	1300	-4
5	100	180	2340	790	41	1850	-6

^a Butyl rubber A contained 1.5 parts sulfur and 5 parts ZnO.

^b Blends were compounded as follows: gum stock, 100; Captax, 0.5; ZnO, 5; stearic acid, 2; sulfur, 2; Furnex Beads, 30; Tuads, 1. Cured in 4 × 4 × 0.032 inch molds.

Apparently blending with Butyl rubber (and presumably certain other synthetics) constitutes a convenient method of lowering the brittle points of polyethyl acrylate vulcanizates. Other methods of lowering the brittle point consist in using plasticizer or in copolymerizing ethyl acrylate with suitable monomers such as *n*-butyl acrylate.

Table VI. Vulcanization of Ethyl Acrylate-Chloropropyl Acrylate Copolymer with Various Agents^a

Compound No.	1 ^b	2	3	4	5 ^b	6	7	8	9	10	11	12
Recipe, parts	0.5	0.5	0.5	0.5	0.5	0.38	..	0.5
Rotax	10	10	10	10	5	10	10	10	10	10	..	10
ZnO	2	2	2	2	3	2	2	2	2	2	..	2
Stearic acid	2	2	2	2
Sulfur	30	50	50	75	30	30	30	30	30	30	30	1
Furnex Beads	1	1	1	1	..	1	0.75
Tuads	..	6	10	20
Plasticizer SC	10
Red lead	2
Quinone dioxime	0.5	..	0.5
Cuprax	1	1
Cumate	1
Polyac	3
Tegul OS	4	..
p-Dinitrobenzene	10	..
Litharge	80
Witcarb R
Curing time, min.	180	240	360	240	60	180	300	300	300	240	360	240
Curing temp., ° F.	312	298	298	298	298	298	298	298	298	298	298	298
Tensile, lb./sq. in.	1210	1170	1190	880	1530	1490	1370	1440	1460	980	1340	1280
Modulus at 600%	830	1080	730	490	1450	660	1070	990	1180	370	..	1240
Ultimate elongation, %	790	690	690	880	650	940	740	790	700	920	560	610
Shore A hardness	48	46	40	40	55	40	43	43	41	38	35	47
Permanent set, %	25.5
At break	13.7	34.9
After 10 min.	21.4	1400	1014	1138	1022	902	750	780	..
Tensile product	956	806	822	774	994	1400	1014	1138	1022	902	750	780

^a 100 parts copolymer (prepared in experiment 8, Table III) used. With exception of experiments 1 and 5, compounded mixtures were cured in 4 × 4 × 0.023 inch molds.
^b Compounded mixtures cured in 6 × 6 × 0.075 inch molds.

MISCELLANEOUS VULCANIZATION RECIPES

Samples of copolymer prepared from ethyl acrylate and chloropropyl acrylate (experiment 8, Table III), were vulcanized with various agents, and the vulcanizates were compared with products obtained with the standard quinone dioxime and sulfur-Tuads recipes.

Both Cuprax and Cumate (cupric salt of mercaptobenzothiazole and cupric diethyldithiocarbamate, respectively) were effective in promoting sulfur vulcanization (Table VI, experiments 6, 7, and 8). The combination of Cuprax and Tuads gave vulcanizates that were superior to those obtained with combinations of Rotax and Tuads, Rotax and Cumate, and Cuprax and Cumate. Polyac (14) caused vulcanization in the absence of sulfur and gave vulcanizates which compared favorably with those prepared by other recipes. The dinitrobenzene litharge combination also gave satisfactory vulcanizates (experiment 11, Table VI). The vulcanizate obtained with Tegul OS, an organic sulfur compound, Rotax, and Tuads (experiment 10) had high elongation but relatively low tensile strength.

Considerable quantities of plasticizers were used in experiments 2, 3, and 4. In the presence of increased amounts of carbon black the plasticizer decreased tensile strength and hardness while increasing the elongation. Witcarb R (calcium carbonate) functioned as a reinforcing agent when used instead of carbon black.

Although the study of compounding and vulcanization is still in the preliminary stage, the results obtained show that certain saturated acrylic resins can be vulcanized, reinforced, and modified with a variety of agents.

PROPERTIES OF VULCANIZED ACRYLIC RESINS

As Figure 1 shows, the copolymer of ethyl acrylate and 5% chloropropyl acrylate has a tensile strength of approximately 1700 pounds per square inch (cured in 6 × 6 × 0.075 inch molds without cellophane sheets) and an elongation of 500%. Higher tensile values may be obtained by sacrificing elongation and presumably with different blacks or higher loading, as shown above. The stress-strain curve of a quinone dioxime vulcanizate is roughly comparable with those of other synthetic elastomers (2) up to about 400% elongation (Figure 1).

The tear strength by the crescent tear test is about 220 pounds per inch. The permanent set is frequently 20% or less. The brittle point is approximately 0°, -15°, or -50° C., depending upon whether methyl acrylate, ethyl acrylate, or *n*-butyl acrylate is the principal monomer.

The polymers are readily milled without softeners or plasticizers. Different compounding recipes can be used, and several blacks and pigments, such as iron oxide, zinc oxide, and calcium carbonate, can be used as reinforcing agents. The copolymers are soluble in organic solvents, and synthetic rubber cements can be prepared from them.

The vulcanizates have the advantages of resistance to oxygen and aging, which one would expect to find in essentially saturated materials. The acrylic elastomers contain a high proportion of oxygen and are resistant to some oils, particularly those that are paraffinic.

Although in some respects vulcanized acrylic resins do not compare favorably with certain other synthetic elastomers, they have several advantages. The monomers can be made from several raw materials, including whey (5), molasses, corn, sugar, petroleum, and coal. Moreover, more than twice as much acrylic elastomer as elastomers of the butadiene types can be made from carbohydrates.

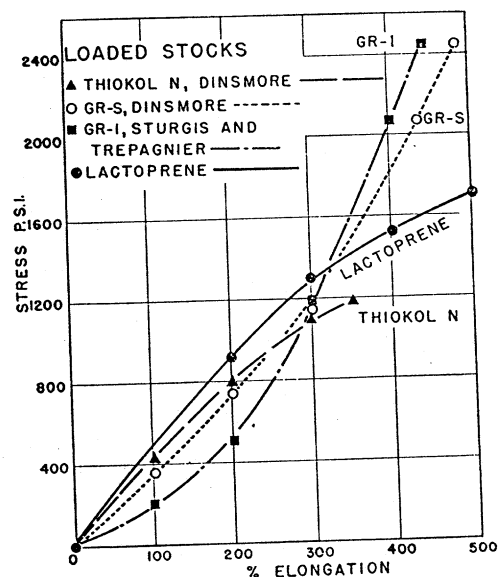


Figure 1. Stress-Strain Curves

Another advantage of acrylic elastomer is that the polymerization can be carried out in simple equipment. Since ethyl acrylate boils at 99° C. at atmospheric pressure, high-pressure reaction vessels are not needed. The time required is short, and polymerization is carried to completion. Polyfunctional monomers are not required, and consequently premature cross linking and its attendant disadvantages are avoided. Any one of several acrylic esters can be used, or two or more acrylic esters can be copolymerized.

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